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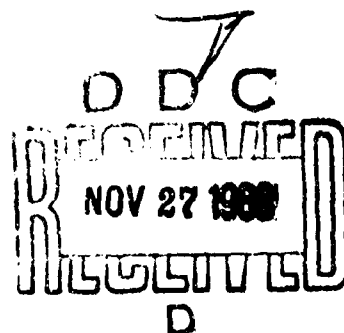
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DEPARTMENT OF THE ARMY  
Fort Detrick  
Frederick, Maryland

## OXIDATION-REDUCTION POTENTIAL AND ELECTRONIC STRUCTURE OF THE CHARGE TRANSFER COMPLEX

[Following is a translation of an article by Mme Andree Goudot, presented at the 27 February 1961 meeting of the French Academy of Sciences and published in the French-language periodical Comptes rendus de l'Academie des Sciences (Reports of the Academy of Sciences), Vol 252, 1961, pages 1521-1523, under the subject heading of Theoretic Biophysics.]

We find, in the enzymatic catalysis of the cupric polyphenoloxidases, two typical examples of charge transfer complexes in which a cupric cation may act on an  $O_2$  molecule, either as an oxidizer or as a reducer. The coordination atoms of the diphenols control the direction of the reaction.

When a metallic cation has an oxidation-reduction potential such as  $Mn^+ = M(n+1)^+ + e^- < 0$ , it tends to go back into its lowest state of valence by capturing an electron. In the hydrated state this cation is an oxidizer. In the formation of a complex: 1. if it is bound to molecules whose coordination atoms are strongly electronegative, the oxidation-reduction potential will decrease, making this complex more oxidizing than the free cation. It may then capture an electron more easily, in order to stabilize the metallic cation in its lowest state of valence; 2. if it is bound to molecules whose coordination atoms are weakly electronegative (strongly donor), the oxidation-reduction potential of the complex will increase with relation to the potential of the free cation. If it is less negative, it is less oxidizing. It may even be that the equilibrium is inverse and that the oxidation-reduction potential of the complex has become sufficiently positive to be a reducer. The metallic cation can then be stabilized in a higher state of valence.

These two extreme cases are found in catalyses of substrates by  $O_2$  with the aid of cupric polyphenoloxydases.

The standard oxidation-reduction potential for  $Cu^+ = Cu^{2+} + e^-$  is  $E_0 = -0.153$  ev;  $Cu^{2+}$  has only nine 3d electrons instead of 10. Therefore, it has a non-saturated  $3d_{x^2-y^2}$  orbit, for it is occupied by a single electron.

It can be considered, in the charge transfer complex, that the divalent cation is joined to the enzyme by two bonds and that, in the presence of a substrate, a saturated complex of hybridization 4 is formed with the aid of two available hybrid bonds.

The two types of cupric polyphenoloxydases considered are: the o-polyphenoloxydase and the p-polyphenoloxydase (J. Roche, Le rôle des métaux dans la structure et l'activité des enzymes / The Role of Metals in the Structure and Activity of Enzymes, Paris: Hermann et Cie., 1946) that differ by their atoms of coordination with  $Cu^{2+}$ .

1. o-polyphenolynase. Extracted from potatoes, it catalyzes the oxidation by the molecular oxygen of the o-diphenols and triphenols that lead to quinonic derivatives (Fig. 1):

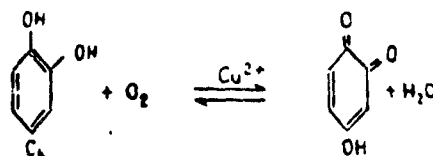


Figure 1

The  $Cu^{2+}$  is joined by two bonds to the enzyme and is bound to the pyrocatechol by the O atoms of the phenol groups. Since these atoms are strongly electronegative, they come under the first case considered. That is to say that the oxidation-reduction potential of the complex that is formed must decrease by making it more oxidizing than the free cation. Now, the complex that is formed is of hybridization  $4s 4p^3$ , in which the orbits of free bonds are thus saturated in order to receive a pair of electrons. In order to be bound to this molecule, in the presence of  $O_2$ , the central cation can only receive a bonding electron in the  $3d_{x^2-y^2}$

orbit which is not saturated, because it contains only one 3d electron. This internal orbit, then, contains a pair of bonding electrons, one of which belongs to the cation and the other comes from O<sub>2</sub>. The complex becomes temporarily a 3d 4s 4p<sup>3</sup> cupreous complex.

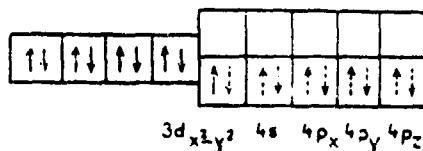


Figure 2

The central cation is temporarily stabilized in the lowest state of valence Cu<sup>+</sup>. While the two O atoms, with a positive charge, repel each other:



The calculation of the charges, in the complex stabilized in the cupreous state, shows that the peak in position 4 has a higher negative charge than in the cupric complex. It is, then, -0.73. It is to be understood that the O atom that is not bound to the central cation and that is dissociated from O<sub>2</sub> becomes fixed at this peak. The electron that is given up in 3 d<sub>x<sup>2</sup>-y<sup>2</sup></sub> can resonate depending on the +X and -X bonds according to which the diphenol bond groups should be found. Then the reaction shown in Figure 1 can occur.

2. p-polyphenoloxidase. It accomplishes oxidation of p-phenyldiamine in the presence of O<sub>2</sub>. We examine the cupric enzyme in the reaction (Fig. 3).

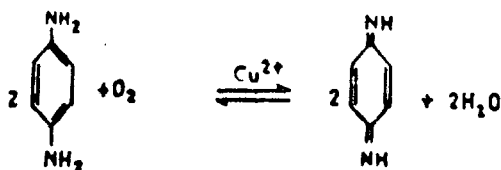


Figure 3

The N bonding atoms belong to amino donor groups. Therefore, this is the second case, in which the redox potential of the complex increases in relation to the redox potential of the hydrated cation. Therefore, it is certainly less oxidizing and the study of the formation of the hybridization complex will show us that it has even become a reducer.

With bonding atoms that belong to weakly electronegative groups, a cupric complex is formed by internal orbit  $3d\ 4s\ 4p^2$ . In order to free the last  $3d$  orbit, the ninth electron that occupied it is raised to an antibonding orbit.

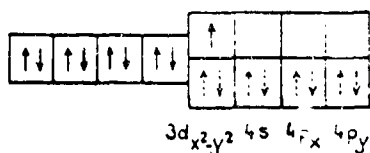


Figure 4

The  $O_2$  molecule is able to utilize the  $4p_z$  external orbit for a weak bond with the metallic cation. Moreover, the  $O_2$  molecule may capture the ninth  $3d$  electron and the result is an  $O_2^-$  ion. The complex, then, is definitely reductive and the central cation is stabilized transitorily in the abnormal  $Cu^{3+}$  state:



Since the p-phenyldiamine bonding atoms are positive, the reaction shown in Figure 3 may occur.

Comment. The action mechanism of o-polyphenolynase should be compared with the action mechanism of cytochrome oxidase (A. Goudot, Cahiers de Physique [Physics Notes], Oct 1961; Comptes rendus [Reports (of the Academy of Sciences)], Vol 251, 1960, p 1194): one  $O_2$  electron is given off in a  $3d_{x^2-y^2}$  orbit for the first one in the  $3d_{z^2}$  orbit for the second one.

The redox potential of the cytochrome is around -0.26 ev and the redox potential of  $Fe^{2+} = Fe^{3+} + e^-$  corresponds to  $E_0 = 0.771$  ev. Therefore, it is less oxidizing but it is sufficiently oxidizing to bring the central cation transitorily back to the ferrous state.

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